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(54) Title: DISPERSANTS, COMPOSITIONS AND USE <div style="text-align: center;"> $\left(T - \left(O - A - CO \right)_n \right)_p - Z \quad (1)$ </div>			
(57) Abstract <p>A dispersant of formula (1) wherein T is hydrogen or a polymerisation terminating group, A is C₈₋₂₀-linear alkylene or alkenylene, Z is the residue of a polyamine or polyimine preferably with average molecular weight from 500 to 600,000, n is from 2 to 10, p is not less than 2, and the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1. The dispersant of formula (1) is particularly useful for dispersing particulate solids in organic media. Compositions comprising a particulate solid and a dispersant of formula (1) are also provided, along with dispersions and milibases comprising a dispersant of formula (1), a particulate solid and an organic medium.</p>			

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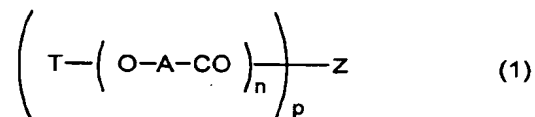
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DISPERSANTS, COMPOSITIONS AND USE

The present invention relates to novel dispersants, to compositions containing the dispersants in an organic medium together with a particulate solid and to the use of such dispersants in the preparation of paints, impact printing inks, multimedia tinters, paints containing aqueous based tinters and the coloration of plastics materials.

US 4,224,212 discloses dispersants which are the reaction product of a polyhydroxycarboxylic acid such as poly(12-hydroxystearic acid) (hereinafter PHS) or polyricinoleic acid (hereinafter PRA) with a polyalkyleneimine such as polyethyleneimine (hereinafter PEI), including their acid salts and quaternary ammonium salts. In the form of their free bases, these dispersants all contain a maximum of four parts by weight of either PHS or PRA for each part of PEI. It has now been found that superior dispersants can be made using a higher amount of polyhydroxycarboxylic acid.

According to the present invention there is provided a dispersant of formula 1



wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene or alkenylene;

Z is the residue of a polyamine or polyimine;

n is from 2 to 10;

p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1.

When T is a polymerisation terminating group, it is preferably the residue of a carboxylic acid of formula T-COOH wherein T may be aromatic, heterocyclic, alicyclic or preferably aliphatic which is optionally substituted by halogen, C₁₋₄-alkoxy, hydroxy and/or ether groups. Preferably, T is unsubstituted. When T is aliphatic, it may be linear or branched, saturated or unsaturated but is preferably linear, saturated alkyl.

The total number of carbon atoms in T can be as high as 50 but it is preferred that T contains not less than 8, more preferably not less than 12 and especially not less than 14 carbon atoms. It is also preferred that T contains not greater than 30, more preferably not greater than 25 and especially not greater than 20 carbon atoms.

Preferably A contains not less than 10, more preferably not less than 12 and especially not less than 14 carbon atoms.

The integer n is preferably not less than 3 and especially not less than 4. It is also preferred that n is not greater than 8 and especially not greater than 6.

The integer p is preferably not greater than 2000 and especially not greater than 1000.

The weight ratio of $(T-(O-A-CO)_n)_p$ to Z is preferably not less than 7:1, more preferably not less than 8:1 and especially not less than 9:1. It is also preferred that the weight ratio of $T-(O-A-CO)_n)_p$ to Z is not greater than 17:1, more preferably not greater than 15:1 and especially not greater than 13:1. Particularly useful effects have been obtained where the weight ratio of $(T-(O-A-CO)_n)_p$ to Z is from 10:1 to 15:1 and especially from 10:1 to 13:1.

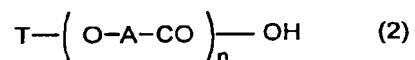
Z is preferably the residue of polyallylamine, polyvinylamine, more preferably poly(C_{2-4} -alkyleneimine) (hereinafter PAI) and particularly poly(ethyleneimine) (PEI).

Linear polyethyleneimines can be prepared by hydrolysis of poly (N-acyl) alkyleneimines as described by Takeo Saegusa et al in *Macromolecules*, 1972, Vol. 5, page 4470. Branched polyethyleneimines of differing molecular weight are available from BASF and Nihon Shokubai. Polyallylamine and poly (N-alkyl) allylamines of differing molecular weight are available from Nitto Boseki. Polyvinylamines are available from Mitsubishi Kasei. Poly (propyleneimine) dendrimers are available from DSM Fine Chemicals and poly (amidoamine) dendrimers are available as "Starburst" dendrimers from Aldrich Chemical Company.

The PAI may be linear or branched.

The polyamine or polyimine preferably has a weight-average molecular weight from 500 to 600,000, more preferably from 1,000 to 200,000, even more preferably from 1,000 to 100,000 and especially from 5,000 to 100,000.

The dispersant according to the invention (hereinafter The Dispersant) is obtainable by reacting the polyamine or polyimine with two or more polyoxyalkylenecarbonyl or polyoxyalkenylenecarbonyl (both hereinafter POAC) chains containing a free carboxylic acid of formula 2



wherein T, A, and n are as defined hereinbefore. The acid of formula 2 is hereinafter referred to as a TPOAC acid.

The number-average molecular weight (M_n) of the TPOAC acid is preferably not less than 500 and especially not less than 800. It is also preferred that the number-average molecular weight of the TPOAC acid is not greater than 3,000 and especially not greater than 2,000.

Whereas it is preferred to prepare The Dispersant by reacting a TPOAC acid with a polyamine or polyimine, The Dispersant may also be prepared by reacting the polyamine or polyimine with a hydroxy carboxylic acid and subsequently reacting the free hydroxy group with more hydroxy carboxylic acid in order to build the POAC chain.

Some commercial sources of hydroxy carboxylic acids contain carboxylic acids which are free from hydroxy groups as an impurity. Consequently, when such sources of hydroxy carboxylic acids are used to prepare The Dispersants it is not necessary to add a separate polymerisation terminating compound since the carboxylic acid which is free from hydroxy groups can fulfil this function.

The Dispersants are obtainable by reacting the polyamine or polyimine with a TPOAC acid at a temperature between 50 and 250°C and preferably in an inert atmosphere. Preferably, the temperature is not less than 80°C and especially not less than 100°C. In order to minimise charring of The Dispersant, the temperature is preferably not greater than 150°C.

The TPOAC acid may be prepared using similar conditions to those employed when reacting the TPOAC acid with the polyamine or polyimine. However, it is preferred to include an esterification catalyst such as a tetra-alkyl titanate, for example tetrabutyltitanate, a zinc salt of an organic acid, for example zinc acetate, a zirconium salt of an aliphatic alcohol, for example zirconium isopropoxide, toluene sulphonic acid or a strong organic acid such as a halo acetic acid, for example trifluoro acetic acid. The polymerisation is generally carried out at temperatures between 150 and 180°C.

When The Dispersant is prepared by reacting the polyamine or polyimine with a hydroxy carboxylic acid, the reaction conditions employed are preferably the same as those used for reacting a TPOAC acid with a polyamine or polyimine. Subsequent building of the POAC chain is preferably carried out under conditions similar to those used for preparing the TPOAC acid.

The inert atmosphere may be provided by any gas which does not react with The Dispersant or with the starting materials and includes the inert gases of the Periodic Table and especially nitrogen.

Particularly useful effects have been obtained with dispersants of formula 1 wherein the TPOAC acid is obtained from 12-hydroxystearic acid, optionally containing stearic acid as polymerisation terminating group with a number-average molecular weight between 800 and 2,000 and Z is the residue of PEI having a number-average molecular weight of from 5,000 to 100,000.

As noted hereinbefore, The Dispersants are particularly useful for dispersing a particulate solid in an organic medium.

According to a further aspect of the invention there is provided a composition comprising a particulate solid and a dispersant of formula 1.

According to a still further aspect of the invention there is provided a dispersion comprising a dispersant of formula 1, a particulate solid and an organic medium.

The solid present in the dispersion may be any inorganic or organic solid material which is substantially insoluble in the organic medium at the temperature concerned and which it is desired to stabilise in a finely divided form therein.

Examples of suitable solids are pigments for solvent inks; pigments, extenders and fillers for paints and plastics materials; dyes, especially disperse dyes; optical brightening agents and textile auxiliaries for solvent dyebaths, inks and other solvent application systems; solids for oil-based and invert-emulsion drilling muds; dirt and solid particles in dry cleaning fluids; particulate ceramic materials; magnetic materials and magnetic recording media, and biocides, agrochemicals and pharmaceuticals which are applied as dispersions in organic media.

A preferred solid is a pigment from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter headed "Pigments". Examples of inorganic pigments are titanium dioxide, zinc oxide, Prussian blue, cadmium sulphide, iron oxides, vermilion, ultramarine and the chrome pigments, including chromates, molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, disazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphenyldioxazine, quinacridone, perylene, diketopyrrolopyrrole and phthalocyanine series, especially copper phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon blacks, although strictly inorganic, behave more like organic pigments in their dispersing properties. Preferred organic pigments are phthalocyanines, especially copper phthalocyanines, monoazos, disazos, indanthrones, anthranthrones, quinacridones and carbon blacks.

Other preferred solids are: extenders and fillers such as talc, kaolin, silica, barytes and chalk; particulate ceramic materials such as alumina, silica, zirconia, titania, silicon nitride, boron nitride, silicon carbide, boron carbide, mixed silicon-aluminium nitrides and metal titanates; particulate magnetic materials such as the magnetic oxides of transition metals, especially iron and chromium, e.g. $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and cobalt-doped iron oxides, calcium oxide, ferrites, especially barium ferrites; and metal particles, especially metallic iron, nickel, cobalt and alloys thereof; and agrochemicals such as the fungicides flutriafen, carbendazim, chlorothalonil and mancozeb.

The organic medium present in the dispersions of the invention is preferably a polar organic medium or a substantially non-polar aliphatic or aromatic hydrocarbon or halogenated hydrocarbon including mixtures thereof. By the term "polar" in relation to the organic medium is meant an organic liquid or resin capable of forming moderate to strong bonds as described in the article entitled "A Three Dimensional Approach to Solubility" by Crowley et al in Journal of Paint Technology, Vol. 38, 1966, at page 269. Such organic media generally have a hydrogen bonding number of 5 or more as defined in the abovementioned article.

Examples of suitable polar organic liquids are amines, ethers, especially lower alkyl ethers, organic acids, esters, ketones, glycols, alcohols and amides. Numerous specific examples of such moderately strongly hydrogen bonding liquids are given in the book entitled "Compatibility and Solubility" by Ibert Mellan (published in 1968 by Noyes Development Corporation) in Table 2.14 on pages 39-40 and these liquids all fall within the scope of the term polar organic liquid as used herein.

Preferred polar organic liquids are dialkyl ketones, alkyl esters of alkane carboxylic acids and alkanols, especially such liquids containing up to, and including, a total of 6 carbon atoms. As examples of the preferred and especially preferred liquids there may be mentioned dialkyl and cycloalkyl ketones, such as acetone, methyl ethyl ketone, diethyl ketone, di-isopropyl ketone, methyl isobutyl ketone, di-isobutyl ketone, methyl isoamyl ketone, methyl n-amyl ketone and cyclohexanone; alkyl esters such as methyl acetate, ethyl acetate, isopropyl acetate, butyl acetate, ethyl formate, methyl propionate, methoxy propylacetate and ethyl butyrate; glycols and glycol esters and ethers, such as ethylene glycol, 2-ethoxyethanol, 3-methoxypropylpropanol, 3-ethoxypropylpropanol, 2-butoxyethyl acetate, 3-methoxypropyl acetate, 3-ethoxypropyl acetate and 2-ethoxyethyl acetate; alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol and dialkyl and cyclic ethers such as diethyl ether and tetrahydrofuran.

The substantially non-polar, organic liquids which may be used, either alone or in admixture with the aforementioned polar solvents, are aromatic hydrocarbons, such as toluene and xylene, and halogenated aliphatic and aromatic hydrocarbons, such as trichloro-ethylene, perchloroethylene and chlorobenzene and particularly aliphatic and aromatic hydrocarbons, especially those having at least 6 carbon atoms, such as refinery distillation products and by-products, including mixtures thereof.

Examples of suitable polar resins, as the medium for the dispersion form of the present invention, are film-forming resins such as are suitable for the preparation of inks, paints and chips for use in various applications such as paints and inks. Examples of such resins include polyamides, such as Versamid™ and Wolfamid™, and cellulose ethers, such as ethyl cellulose and ethyl hydroxyethyl cellulose. Examples of paint resins include short oil alkyd/melamine-formaldehyde, polyester/melamine-formaldehyde, thermosetting acrylic/melamine-formaldehyde, long oil alkyd and multi-media resins such as acrylic and urea/aldehyde.

If desired, the dispersions may contain other ingredients, for example resins (where these do not already constitute the organic medium) binders, fluidising agents (such as those described in GB-A-1508576 and GB-A-2108143), anti-sedimentation agents (such as those described in WO 96/14344), plasticisers, levelling agents and preservatives.

Preferably, the organic medium is a substantially non-polar organic liquid and especially an aliphatic or aromatic hydrocarbon, or mixture thereof.

The dispersions typically contain from 5 to 95% by weight of the solid, the precise quantity depending on the nature of the solid and the quantity depending on the nature of the solid and the relative densities of the solid and the organic medium. For example, a dispersion in which the solid is an organic material, such as an organic pigment, preferably contains from 15 to 60% by weight of the solid whereas a dispersion in which the solid is an inorganic material, such as an inorganic pigment, filler or extender, preferably contains from 40 to 90% by weight of the solid based on the total weight of dispersion.

The dispersion may be obtained by any of the conventional methods known for preparing dispersions. Thus, the solid, the organic medium and the dispersant may be mixed in any order, the mixture then being subjected to a mechanical treatment to reduce the particles of the solid to an appropriate size, for example by ball milling, bead milling, gravel milling or plastic milling until the dispersion is formed. Alternatively, the solid may be treated to reduce its particle size independently or in admixture with either the organic medium or the dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If the composition is required in dry form, the liquid medium is preferably volatile so that it may be readily removed from the particulate solid by a simple separation means such as evaporation. It is preferred, however, that the dispersion comprises the liquid medium.

If the dry composition consists essentially of the dispersant and the particulate solid, it preferably contains at least 0.2%, more preferably at least 0.5% and especially at least 1.0% dispersant based on weight of the particulate solid. Preferably the dry composition contains not greater than 100%, preferably not greater than 50%, more preferably not greater than 20% and especially not greater than 10% by weight based on the weight of the particulate solid. For example, a dry composition containing 100% dispersant based on the weight of the particulate solid, will contain equal weight amounts of dispersant and the particulate solid.

As described hereinbefore, the dispersants of the invention are particularly suitable for preparing mill-bases where the particulate solid is milled in a liquid medium in the presence of The Dispersant and optionally a film-forming resin binder.

Thus, according to a yet still further aspect of the invention there is provided a mill-base comprising a particulate solid, dispersant of formula 1, film-forming resin and a liquid medium.

Typically, the mill-base contains from 20 to 70% by weight particulate solid based on the total weight of the mill-base. Preferably, the particulate solid is not less than 30 and especially not less than 50% by weight of the mill-base.

The amount of resin in the mill-base, when present, can vary over wide limits but is preferably not less than 10%, and especially not less than 20% by weight of the

continuous/liquid phase of the mill-base. Preferably, the amount of resin is not greater than 50% and especially not greater than 40% by weight of the continuous/liquid phase of the mill-base.

5 The amount of dispersant in the mill-base is dependent on the amount of particulate solid but is preferably from 0.5 to 5% by weight of the mill-base.

Dispersions and mill bases containing the dispersants of the invention are particularly suitable for use in paints, especially high solids paints, impact printing inks, especially off-set, gravure, roller and screen inks, and non-aqueous ceramic processes, especially tape-coating, doctor-blade, extrusion and injection moulding type processes.

10 The Dispersants may also be used in the preparation of multimedia tinter paints and impact printing inks where one or more pigments are dispersed in an organic liquid medium, especially a substantially non-polar organic liquid.

Furthermore, The Dispersants may also be used in the preparation of paints and impact printing inks which contain a tinter pigment in either water and/or a polar organic liquid. The tinter pigment may belong to any class of pigments and is used to impart shade changes to a base paint or impact printing ink containing a base pigment. Preferably, the base pigment in such paints is a white pigment such as titanium dioxide. The tinter pigment is generally added as a dispersion in water and/or polar solvent, especially a glycol such as ethyleneglycol. The dispersant used to disperse the tinter pigment in water and/or polar solvent is preferably a dispersant other than a dispersant of formula 1. The Dispersant is used to disperse the base pigment in a substantially non polar liquid. The amount of water and/or polar solvent containing the tinter pigment is preferably less than 10%, more preferably less than 5% and especially less than 3% based on the weight of the base paint or impact printing ink which contains the base pigment and resin dispersed in a substantially non-polar organic liquid.

25 The Dispersants may also be used to disperse particulate solids, especially pigments for use in the plastics industries. They are particularly suited for dispersing pigments into liquid media for the colouration of plastics materials, especially thermoplastic materials, such as polyolefins, polyesters, polyamides, polyurethanes, polystyrenes and PVC and highly suited to preparing coloured master batches which are subsequently mixed with non-coloured plastics materials prior to the fabrication of formed articles.

When The Dispersants are used to prepare impact printing inks, the inks are preferably off-set, gravure, roller and screen inks.

35 The Dispersants have also been found useful in preparing dispersions, millbases, paints and impact printing inks where a metal complex of crude phthalocyanine, for example, copper phthalocyanine is milled in a high boiling aliphatic hydrocarbon solvent at elevated temperature, for example between 50°C and 150°C.

As noted hereinbefore, The Dispersants exhibit advantage over those described in US 4,224,212. Thus, for example, they result in pigment dispersions in non-polar organic liquids which exhibit superior fluidity and lower viscosity, thus enabling higher pigment loadings. Also, paints and impact printing inks made using these dispersants also exhibit advantage, for example, superior drying time.

The invention is further illustrated by the following examples wherein all references to amounts are in parts by weight unless indicated to the contrary.

Examples

Preparation of Dispersants

Example 1 PHS : PEI (5:1)

Poly(12-hydroxystearic acid) (PHS) (MW 1600, 55 parts, Polyester A, Agent A, US 4,224,212) was heated to 120°C with stirring under a nitrogen atmosphere. Polyethyleneimine (MW 10,000, 11 parts, SP200 ex Nippon Shokhubai) was added and the reactants stirred under nitrogen at 120°C for a further 6 hours. On cooling, the product was obtained as a brown viscous liquid (60 parts). This is Dispersant 1.

Examples 2 to 9

Example 1 was repeated except using the amounts of PHS and PEI indicated in Table 1 below. The Dispersants were obtained as brown viscous liquids.

Table 1

Example	Dispersant	Amount of PHS	Amount of PEI	Weight Ratio of PHS : PEI
2	2	49	7	7:1
3	3	40	5	8:1
4	4	54	6	9:1
5	5	50	5	10:1
6	6	48	4	12:1
7	7	45	3	15:1
8	8	51	3	17:1
9	9	50	2.5	20:1

Comparative Example A PHS : PEI (4:1)

This was prepared in similar manner to Example 7/Agent H of US 4,224,212. Polyethyleneimine (PEI) (MW 10,000, 30 parts as 50% solution in water as Polymin P ex BASF) was heated at 100°C under reduced pressure to remove the water.

Poly(12-hydroxystearic acid) (MW 1600, 60 parts, Polyester A, Agent A, US 4,224,212) was stirred at 120°C under a nitrogen atmosphere. The anhydrous PEI was added and the reactants stirred under nitrogen for a further 25 minutes at 120°C. The product was obtained as a light brown viscous liquid which cooled to a clear gel (85 parts). This is Dispersant A.

Comparative Example B PHS : PEI (8:1) quaternised with dimethylsulphate

This was prepared in similar manner to Example 4/Agent E of US 4,224,212. Polyethyleneimine (PEI) (MW 10,000, 18.2 parts as 50% solution in water as Polymin P ex BASF) was heated at 100°C under reduced pressure to remove the water.

Poly(12-hydroxystearic acid) (MW 1600, 72.8 parts, Polyester A, Agent A, US 4,224,212) was stirred at 120°C under a nitrogen atmosphere. The anhydrous PEI was added and the reactants stirred under nitrogen for a further 2 hours at 150°C. The mixture was cooled to 100°C. The base equivalent was measured as 767.67, therefore dimethyl sulphate (MW 126.13, 12.49 parts, equates to 95% of free amines available) was added to the reaction mixture and stirring continued for 1 hour at 100°C. The product was obtained as a highly viscous liquid which cooled to a gel (80 parts). This is Dispersant B.

Examples 10 to 12

The Dispersant (0.3 parts) listed in Table 2 below was dissolved in a non-polar hydrocarbon solvent (6.6 parts Parasat 29L ex Carless Refining Ltd.) by warming as necessary in an 8 dram glass vial and then allowed to cool. A quaternary ammonium salt of sulphonated copper phthalocyanine (0.1 parts, Solsperse 5000 ex Zeneca Ltd) was added as fluidising agent together with blue pigment (3 parts Monastral Blue BG ex Zeneca Ltd.) and glass beads (3mm, 17 parts). The vials were then sealed and shaken on a horizontal shaker for 16 hours. The beads were then removed and the resulting dispersion assessed for fluidity by handshaking and using an arbitrary assessment scale of A to E (good to bad). A is very fluid, B is fluid and gels after 10 minutes, C is fluid and gels after 60 seconds, D is slightly fluid and gels after shaking by hand and E is a thick immovable gel. The results are given in Table 2 below.

Table 2

Example/Comp. Ex	Dispersant	Ratio of PHS : PEI	Fluidity
10	1	5:1	A
11	2	7:1	A
12	4	9:1	A
Control	A	4:1	B

Example 13

The Dispersant (0.72 parts) was dissolved in a hydrocarbon solvent (21.36 parts, Parasat 29L ex Carless Refining Ltd.) by warming and then allowed to cool. A quaternary ammonium salt of sulphonated copper phthalocyanine (0.32 parts, Solspers 5000 ex Zeneca Ltd) was added as fluidising agent followed by blue pigment (9.6 parts Monastral Blue BG ex Zeneca Ltd.) and glass beads (3mm, 125 parts). The pigment dispersion was prepared by milling on a Red Devil Shaker for 45 minutes. After removal of the beads the viscosity of the resultant dispersion was measured on a Bohlin viscometer using a 2.5° cone plate and 15mm diameter. The results are given in Table 3 below.

Table 3

Shear Rate (1/S)	Viscosity (Pas)		
	Example 13 9:1 Dispersant 4	4:1 Dispersant A	8:1 quat Dispersant B
0.038	0.292	0.811	1.789
0.10	0.094	0.483	0.780
0.18	0.063	0.371	0.500
0.30	0.042	0.286	0.328
0.49	0.020	0.202	0.218
0.84	0.020	0.157	0.154
1.41	0.016	0.121	0.110
2.40	0.013	0.097	0.080

Footnote to Table 3

Dispersant A is PHS : PEI (4:1) prepared in Comparative Example A

Dispersant B is PHS : PEI (8:1) quaternised with dimethylsulphate prepared in Comparative Example B

Example 14

Example 13 was repeated except using dispersant (1.6 parts), hydrocarbon solvent (18.4 parts Parasat 29L ex Carless Refining Ltd.), a quaternary ammonium salt of sulphonated copper phthalocyanine (0.8 parts Solspers 5000 ex Zeneca Ltd) and crude blue Cu phthalocyanine pigment (11.2 parts ex Phthalchem USA). After milling on the Red Devil shaker for 90 minutes, the viscosity was again measured using a Bohlin viscometer using a 2.5° cone plate and 15mm diameter. The results are given in Table 4 below.

Table 4

Shear Rate (1/S)	Viscosity (Pas)		
	Example 14 Dispersant 4	Dispersant A	Dispersant B
0.038	1.58	14.39	16.55
0.10	0.98	6.75	6.43
0.18	0.72	3.47	3.30
0.30	0.52	1.83	1.76
0.49	0.38	1.10	1.11
0.84	0.29	0.67	0.70
1.41	0.22	0.44	0.43
2.40	0.16	0.30	0.23

Footnote to Table 4

5 Dispersants A and B are as explained in the footnote to Table 3.

Examples 15 to 21

Example 13 was repeated except using Dispersant (0.23 parts), hydrocarbon solvent (6.67 parts Paraset 29L ex Carless Refining Ltd.), fluidising agent (0.1 part Solsperse 5000 ex Zeneca Ltd) and blue pigment (3 parts Monastral Blue BG, ex Zeneca Ltd.) and milling for 16 hours. The fluidity of the resultant dispersions were assessed using the method described in Examples 10 to 12 and the viscosity was again measured using a Bohlin Viscometer. The results are given in Tables 5, 6a and 6b below which show the superiority of dispersants having a higher amount of PHS to PEI than 4:1. The viscosity recorded in Table 6a used a 5° cone plate with 30mm and the viscosity recorded in Table 6b used a 2.5° cone plate and 15mm diameter. Those dispersants wherein the weight ratio of PHS to PEI is between 10:1 and 17:1 are particularly efficacious. The viscosity of millbases containing Dispersants A and B were too high to measure using the Bohlin Viscometer.

Table 5

Example	Dispersant	Weight Ratio of PHS : PEI	Fluidity
15	3	8:1	C/D
16	4	9:1	C/D
17	5	10:1	A/B
18	6	12:1	A/B
19	7	15:1	B
20	8	17:1	B
21	9	20:1	B/C
-	A	4:1	D/E
-	B	8:1 quat	C/D

Footnote to Table 5

5

Dispersants A and B are as explained in the footnote to Table 3.

Fluidity assessment A to E is as explained in Examples 10 to 12.

Table 6a

Shear Rate (1/S)	Viscosity (Pas)						
	Disp. 3 8:1	Disp. 4 9:1	Disp. 5 10:1	Disp. 6 12:1	Disp. 7 15:1	Disp. 8 17:1	Disp. 9 20:1
18	2.37	1.89	0.56	0.84	1.01	1.35	1.95
47	1.16	1.01	0.35	0.36	0.43	0.72	0.93
81	0.80	0.78	0.25	0.29	0.31	0.53	0.66
136	0.54	0.51	0.18	0.22	0.22	0.39	0.45
225	0.36	0.34	0.12	0.14	0.16	0.27	0.32
384	0.28	0.26	0.11	0.12	0.13	0.21	0.25
645	0.21	0.19	0.09	0.09	0.12	0.16	0.19
1096	0.16	0.15	0.08	0.09	0.08	0.13	0.15

10

Cone plate 5° / 30mm.

15

Table 6b

Shear Rate (1/S)	Viscosity (Pas)							
	Disp. 3	Disp. 4	Disp. 5	Disp. 6	Disp. 7	Disp. 8	Disp. 9	Control
0.038	5.32	8.10	4.40	2.60	3.62	4.04	6.06	11.57
0.10	2.09	3.64	1.85	1.40	1.43	1.72	2.62	5.67
0.18	1.36	2.41	1.32	0.82	1.05	1.14	1.73	3.79
0.30	0.99	1.65	0.90	0.56	0.69	0.73	1.20	2.63
0.49	0.65	1.09	0.60	0.32	0.42	0.47	0.79	1.86
0.84	0.53	0.84	0.52	0.29	0.37	0.39	0.64	1.44
1.40	0.41	0.62	0.45	0.25	0.28	0.31	0.52	1.12
2.38	0.33	0.48	0.37	0.21	0.22	0.27	0.43	0.99

Footnote to Table 6b

5 Control is PHS (MW 3,000) : PEI (MW 10,000) (7:2 w/w)

Example 22 PHS : PEI (10:1)

10 Polyhydroxystearic acid (PHS) (MW 1600, 30 parts, Polyester A, Agent A of US 4,224,212) was dissolved in toluene (10 parts) and polyallylamine (6 parts, 50% aqueous solution, Lupasol G100 ex BASF) were stirred at 120°C for 6 hours under a strong stream of nitrogen to remove water formed in the reaction. After cooling, the product was obtained as a clear golden yellow viscous liquid (30 parts). This is Dispersant 10.

Example 23 PHS : PAA (10:1)

15 Polyhydroxy stearic acid (PHS) MW 1600, 30 parts, Polyester A, Agent A of US 4,224,212) was dissolved in toluene (10 parts) and polyallylamine (6 parts, 50% aqueous solution ex Aldrich) was added. The reactants were stirred at 130°C for 16 hours under nitrogen under reflux conditions. The temperature was then raised to 150°C and stirred for 6 hours under nitrogen to remove the water/toluene mixture as an azeotropic mix.
 20 After cooling, the product was obtained as a viscous gum (30 parts). This is Dispersant 11.

Example 24

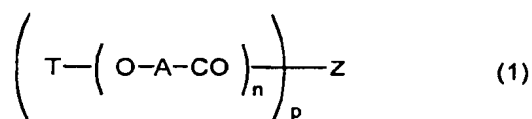
25 Dispersions were prepared as described in Example 13 except using Dispersants 10 and 11. The viscosity was measured using a Bohlin Viscometer equipped with a 2.5° cone face, diameter 15mm. The results are given in Table 7 below.

Tabl 7

Shear Rate (1/S)	Viscosity (Pas)	
	Dispersant 10	Dispersant 11
0.038	3.40	1.63
0.10	1.21	0.86
0.18	0.83	0.54
0.30	0.56	0.32
0.49	0.38	0.17
0.83	0.35	0.16
1.40	0.28	0.15
2.38	0.25	0.12

CLAIMS

1. A dispersant of formula 1



wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene or alkenylene;

Z is the residue of a polyamine or polyimine;

n is from 2 to 10;

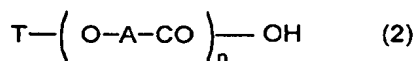
p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1.

2. A dispersant as claimed in claim 1 wherein the polymerisation terminating group is the residue of an aliphatic carboxylic acid T-COOH wherein T contains from 8 to 30 carbon atoms.

3. A dispersant as claimed in either claim 1 or claim 2 wherein the weight ratio of (T-(O-A-CO)_n)_p to Z is from 9:1 to 13:1.

4. A dispersant as claimed in any one of claims 1 to 4 which is obtainable by reacting a polyamine or polyimine with two or more TPOAC acids of formula 2



wherein T, A and n are as defined in claim 1.

5. A dispersant as claimed in claim 4 wherein the TPOAC acid is obtainable by polymerising 12-hydroxystearic acid.

6. A dispersant as claimed in either claim 4 or claim 5 wherein the TPOAC acid has a weight-average molecular weight between 1000 and 2000.

7. A dispersant as claimed in any one of claims 1 to 6 wherein Z is the residue of polyethyleneimine.

8. A composition comprising a particulate solid and a dispersant as claimed in any one of claims 1 to 7.

5 9. A dispersion comprising a particulate solid, an organic medium and a dispersant as claimed in any one of claims 1 to 7.

10. A dispersion as claimed in claim 9 wherein the organic medium is a substantially non-polar organic liquid.

10 11. A millbase comprising a particulate solid, a film-forming resin, an organic medium and a dispersant as claimed in any one of claims 1 to 7.

12. A paint or impact printing ink comprising a pigment, a film-forming resin, an organic medium and a dispersant as claimed in any one of claims 1 to 7.